(12) # EUROPEAN PATENT APPLICATION

(72) Inventor: Suntola, Tuomo
Vasamatie 25
SF-02360 Espoo(FI)
Inventor: Haukka, Suvi
Kymintie 41 A
SF-00560 Helsinki(FI)
Inventor: Kytökivi, Arla
Servin-Maijan tie 6 G 98
SF-02150 Espoo(FI)
Inventor: Lakomaa, Eeva-Liisa
Soukanahde 7 F 116
SF-02360 Espoo(FI)
Inventor: Lindblad, Marina
Kankurinkatu 2 A 18

SF-00150 Helsinki(FI)
Inventor: Hietala, Jukka
Luhtitie 2 B 5
SF-06400 Porvoo(FI)
Inventor: Hokkanen, Harri
Kianeettitie 1 A 28
SF-00420 Helsinki(FI)
Inventor: Knuuttila, Hilkka
Torpparintie 4
SF-06400 Porvoo(FI)
Inventor: Knuuttila, Pekka
Torpparintie 4
SF-06400 Porvoo(FI)
Inventor: Krause, Outi
Kuusitie 22 A 2
SF-04130 Sipoo(FI)
Inventor: Lindfors, Lars Peter
Temppelikatu 10 A
SF-00100 Helsinki(FI)

(74) Representative: Schmidt-Evers, Jürgen,
Dipl.-Ing. et al
Patentanwälte Mitscherlich & Partner,
Steinsdorfstrasse 10
W-8000 München 22(DE)

(54) Method for preparing heterogeneous catalysts of desired metal content.

(57) The present invention concerns a method for preparing heterogeneous catalysts. According to the method, preparation is carried out under such process conditions in which the bonding of compounds from the gas phase onto the surface of a support material is primarily determined by the properties of the support surface. The constituents contained in the reagent are then selectively bonded to the bonding sites of the support material surface, thus forming stable surface bonds. According to the invention, the number of surface-bond sites available for preparing a stable product with surface bonds is controlled by varying the reaction temperature and/or selecting a suitable reagent. The invention makes it possible to control the metal content of the end product at a predetermined level.
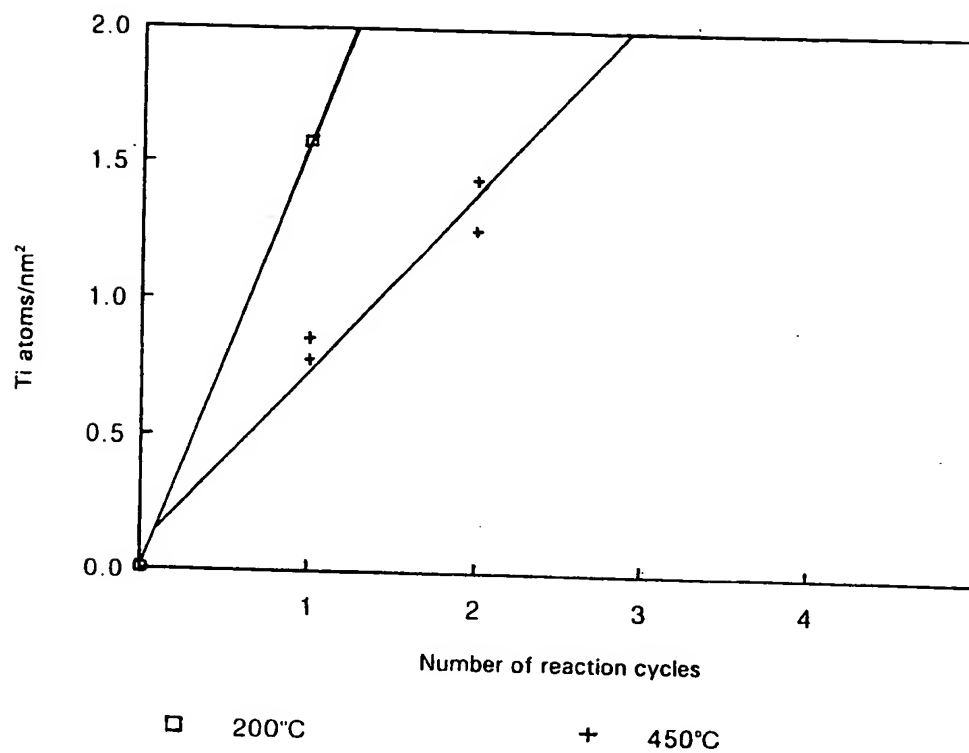
EP 0 525 503 A1

Fig. 1 Content of Ti species in TiO_2 layers.

The present invention relates to a method in accordance with the preambles of claims 1 and 10 for preparing a heterogeneous catalyst comprised of a support material and at least one catalytically active species.

According to the present method, the catalytically active species or a reagent containing its precursor is transferred into a reaction space where it is reacted in vapour phase with the surface of the support material.

When preparing heterogeneous catalysts in the traditional manner, the catalytically active species are bonded to the surface of the support material using, e.g., impregnation, precipitation or ion exchange techniques. The initial reagents here are chemical compounds, generally salts, that are soluble in conventional solvents. The most common solvents used are water and alcohols.

The metal content of the catalysts being prepared is controlled in the impregnation technique by altering the metal compound concentration in the solution and using a certain precalculated volume of the solvent which is then used in toto to impregnate a porous support material.

This traditional method of catalysts preparation is hindered by the great number of different work phases required, whereby the risk of preparation errors increases. The catalyst preparation process is very sensitive to ambient conditions, thus necessitating very accurate control. Another disadvantage is related to the use of solvents. Namely, solvents can often react with the support material causing changes in its surface structure. Furthermore, solvents frequently contain impurities, which may affect the activity of the prepared catalyst.

To avoid the disadvantages of liquid-phase techniques, several different gas-phase techniques have been developed in which the support materials are reacted with gasor vapour-phase reagents containing the catalytically active species or its precursor. When using gas-phase techniques, the content of the metal compound in the final product is conventionally controlled by metering a certain amount of the gas into the reaction space.

Such gas-phase techniques known in the art achieve the control of the average concentration of the metal compound but fail in simultaneously achieving the control of the active species distribution on the support material. A frequently occurring phenomenon is the aggregation of the active species into clusters, so all molecules of the metal species cannot act as catalytically active points.

It is an object of the present invention to overcome the drawbacks of conventional technology and achieve a method suited to the preparation of heterogeneous catalysts having a desired content of the active species.

The invention is based on two basic ideas.

Firstly, the method aims to achieve a situation in which the bonding of the gas-phase materials onto the support material surface is primarily determined by the properties of the support material surface. In the context of the present invention, this property is called the "surface-bond selectivity". Namely, the goal is to achieve such process conditions in which the constituents of the reagent are selectively bonded to the bonding sites available on the support material surface, thus forming permanent surface bonds. Which bonding sites under certain conditions are available for achieving a stable end product is determined by, among other factors, the surface structure of the support material, the reaction temperature and other reaction parameters, as well as the reactivity of the reagent and its bonding energy in the reaction. The principal properties of the support material surface affecting the end result are the structural geometry of the atoms in the support material surface and their electron configuration (that is, the energy potential function of the surface).

The reaction temperature and time applied in the method, as well as other similar conditions, are determined by the support material/reagent pair. Independently of the support material and the reagent, the method according to the invention is, however, characterized in that the surface-bonding selectivity is ensured by maintaining the vapour pressure of the reagent sufficiently high and the reaction time sufficiently long to keep the amount of the reagent at least to the number of surface-bond sites available at a time.

According to the present invention, through the fulfillment of the surface-bonding selectivity requirement, a homogeneous distribution of the active species is achieved by virtue of saturating surface-bond reactions. The utilization of the saturation principle of the surface-bond reactions yields a homogeneous distribution of the active species and simultaneously controls the active species content at a saturation level which is determined by the number of surface-bond sites participating in the reaction. Consequently, the second basic idea of the invention requires that the number of those surface-bond sites which, under the predetermined conditions of set temperature, introduced reagent, and chemical structure of the support material surface, are available to form a stable surface-bond reacted product must at least essentially correspond to the desired content of the catalytically active species in the catalyst being prepared. For this purpose, according to the invention, the number of surface-bond sites is predetermined through two major variables, namely, control of the reaction temperature and/or proper selection of the reagent.

More specifically, the method in accordance with the invention is principally characterized by

what is stated in the characterizing parts of claims 1 and 10.

The invention combines the benefits of surface-bonding selectivity and reaction controllability. Hence, the invention makes it possible to achieve a heterogeneous catalyst whose activity even at a low content of the catalytic metal is as high as that of a catalyst of higher metal content prepared in a conventional manner. Moreover, the metal content of the end product can be accurately controlled at a predetermined level.

The definitions used in the context of the present invention are as follows:

Catalyst reagent refers to an initial reagent which is capable of being converted into gaseous form and then reacting on the support material surface so as to form a catalytically active site or a precursor necessary for generating such a site. The catalyst reagent can be any vapourizable or gaseous compound conventionally used in the preparation of heterogeneous catalysts. Thus, applicable reagent materials include, for example, elemental metals such as zinc, metal compounds such as rhenium oxides, metal halides such as halogenated chromium compounds, tungsten chlorides and oxychlorides, and metal complex compounds such as Cr-(acac)₃ and Mg(thd)₂.

Precursor refers to such available (inactive) initial forms of the catalytically active constituent from which the active species can be obtained by means of an appropriate treatment.

Active species refers to a catalytically active component on the support material surface, whereby the active species can be in the form of, e.g., an atom, ion, molecule, chemical compound or complex compound. Conventionally, the active species is comprised of a metal ion or atom or metal compound bonded to the support material surface.

Support material refers to a material in solid state that provides a surface of at least a relatively large area, capable of bonding the catalytically active species or its compound. The surface area of the support material determined by the BET method typically is in the range from 10 to 1000 m²/g. The support material can be comprised of an inorganic oxide such as silicon oxide (silica gel), aluminium oxide, thorium oxide, zirconium oxide, magnesium oxide, or any of their mixtures. In their inherent form, these support materials are essentially inactive as catalysts. Alternatively, support materials can be employed that inherently act as catalysts in the chemical reaction to be catalyzed. Examples of such support materials are natural and synthetic zeolites. Also inactive support materials having species of a catalytically active material bonded to their surface are considered support materials within the context of the present application. Thus, when preparing bimetal catalysts, the

first catalytic species bonded to the support material surface is defined to form a part of the support surface for the second catalytic species.

Reaction space refers to the space in which the support material and the reagents are interacted with each other.

It is an object of the present invention to combine selective surface bonding with the controllability of the content of the catalytically active species. An essential property of the invention is the manner of maintaining the saturation condition during the surface-bond reaction which is characteristic of the present surface-bond selective method.

The method according to the invention comprises chiefly three phases of which the pretreatment and posttreatment phases are advantageous in some embodiments of the invention, although they are not necessary for the implementation of the basic principle of the invention.

To attain the reaction conditions favourable for the selective surface-bond reaction, all reagents necessary for the pretreatment, the bonding of the catalytically active species, and the posttreatment are introduced into the reaction space in gaseous form, typically one reagent at a time. The vapour pressure of the vapourized catalyst reagent is then maintained sufficiently high and the interaction time of the reaction with the support material surface sufficiently long so that the amount of available reagent is at least as high, or preferably in excess of the amount required to saturate the number of surface-bond sites available on the support material. The excess ratio of the reagent quantity employed to the atomic or molecular layer (known as monolayer) quantity which is necessary for filling all available bonding sites on the substrate material surface is typically in the range from 1 to 100, preferably 1 to 2. The reagent quantity corresponding to the monolayer bonding situation can be computed on the basis of the surface area of the supporting material determined with the help of, e.g., the BET method, and the molecular structure of the surface.

According to the invention, the reaction conditions are created such that the active species of the gas-phase reagent during the reaction with the support material surface can fill absolutely all or essentially all available bonding sites, whereby the saturation of the support material surface is attained at the set reaction temperature.

To prevent condensation of the reagent, the reaction temperature must not be allowed to fall essentially below the temperature necessary for vapourization of the reagent. Condensation of the reagent during its transfer to the reaction space must also be prevented. The initial reagent, its vapour temperature and the temperature used in

the reaction must be selected so that decomposition of the initial reagent and possible condensation of decomposition products are prevented.

Experimental methods can be applied to determine the temperature window, or the temperature span, in which the reaction is advantageously carried out. The lower limit of such span is determined by the condensation temperature of the reagent to be vapourized and the activation energy necessary to attain a desired activation energy to establish a bond to the surface-bond site. This is because the condensation temperature of the catalyst reagent cannot be taken as the lower limit temperature for the bonding reaction if said temperature is too low for imparting to the reagent a sufficient energy to exceed the activation energy. The upper temperature limit is the lower of the following two temperatures: The decomposition temperature of the reagent or the temperature at which the constituent chemisorbed on the support material or its precursor starts to desorb in an essential amount from the advantageous bonding sites. The reagent is selected so that the activation energy necessary for chemisorption is exceeded at a temperature at which desorption from the advantageous bonding sites still remains insignificant. Because the activation and desorption energies are not generally known, the selection of the proper reagent and temperature must be performed experimentally.

The reaction between the vapour of the catalyst reagent and the support material can be carried out at elevated pressure, ambient pressure or partial vacuum. According to a preferred embodiment of the invention, the preparation takes place at a pressure ranging from 0.1 to 100 mbar. An advantage of the partial vacuum is that purity of the reaction space can be improved and the diffusion rate increased. Another preferred approach is to operate at ambient pressure. This permits the use of less complicated equipment. The preparation at ambient pressure is advantageous when the reagent under the reaction conditions has a partial pressure approximating the ambient pressure, preferably greater than 100 mbar.

The reaction time is principally affected by the diffusion of gas molecules into the pores of the support material. Diffusion of gas between the particles of the support material is rapid in comparison with the diffusion into the pores. The reaction time is selected so long as to permit a sufficiently effective interaction of the gas containing the active component of the reagent with the bonding sites of the support material and to achieve saturation of the support material surface. In the tests performed, a reaction time of 0.1 to 10 h, typically 0.5 to 2 h, was found sufficient to achieve this situation when treating support material quantities of 1 to 20 g.

In a preferred embodiment, an inert gas is conducted through a static support material column at a flow rate which remains appreciably smaller than the thermal diffusion rate of the reagent. In particular, the carrier gas flow rate is adjusted so as to be essentially equal to the diffusion rate of the reagent into the pores of the support material under the reaction conditions. This is because the saturation principle permits the use of a low flow rate that assures effective interaction between the reagent and the support material surface. Thence, the individual molecules of the reagent gas can make a plurality of impacts on the surface, which further results in an effective saturation of the bonding sites of the support material without causing a significant macroscopic oversaturation. The typical carrier gas flow rate in this embodiment is approx. 10 cm/min. The verification of the saturation condition can be performed by determination of the active species or precursor content in that part of the ready-made end product which during the reaction has been in the upper part of the support material column (that is, the carrier gas inlet end), and correspondingly, at the lower end of the column (that is, the exit end). If these two contents are equal, saturation conditions have been attained.

A pretreatment is applied to produce a predetermined number of desired bonding sites for the catalytically active species to be bonded. The pretreatment can be performed using a thermal treatment or a chemical treatment or a combination of both.

To optimize the properties of the catalyst, it can be subjected to a posttreatment if desired. This can be implemented using, e.g., a thermal treatment in which the catalyst is heated to a desired temperature which generally is slightly higher than that of the bonding reaction. When the degree of oxidization at the catalytically active point is desired to be altered, the thermal treatment is carried out in oxidizing, or alternatively, reducing conditions. The posttreatment process can also be employed to interact the prepared catalyst with a vapour, e.g., water vapour, which can affect the bonding environment of the active species or a precursor already bonded to the support material surface.

The content of the active species bonded by chemisorption is controlled according to the invention within the scope of the surface-bond selective method via the control of the saturation level, which can be implemented by varying, e.g.:
- the reaction conditions (A),
- the surface (B) participating in the surface-bond reaction, and
- the reagent (C) introduced in gas phase.
The saturation level attained in the surface-bond

EP 0 525 503 A1

reaction is determined by the combined effect of these three partial factors.

The basic control means are provided by the reaction conditions A. The most important control parameter of the reaction conditions is the reaction temperature. The variation limits of the reaction temperature and the effect of their variation is essentially dependent on the surface B and the reagent C participating in the surface-bond reaction. Each combination of B and C is related to a specific temperature window and control range of active species content.

The variation limits of the reaction temperature (temperature window) are set by the requirement of maintaining the saturation conditions. The reaction temperature offers a means for controlling the saturation level if bonding sites of different activation energies or different bonding energies for the reagent C are available on the surface B. If the surface provides bonding sites of a single type only (that is, of identical activation energy and identical bonding energy) for the reagent, the saturation level is independent of the reaction temperature within the temperature window allowable for the reaction.

If the surface has bonding sites of two different activation energy levels E_a1 and E_a2 ($E_a1 < E_a2$) for the reagent, it is possible to find within the reaction's temperature window a threshold temperature (or a temperature span of change) below which bonding sites having the activation energy level E_a1 only are filled, while when the temperature is increased above said temperature, bonds are formed to the sites of both activation energy levels E_a1 and E_a2. Then, the reaction temperature can be employed to select between two different levels of saturation.

If the surface has bonding sites of two different bonding energy levels E_s1 and E_s2 ($E_s1 < E_s2$) for the reagent, it is possible to find within the temperature window of the reaction a threshold temperature (or a temperature span of change) below which bonds formed to the sites of both bonding energy levels E_s1 and E_s2 are retained, and above which only bonds having the bonding energy E_s1 are retained. Also in this case the reaction temperature can be employed to select between two different levels of saturation.

The levels of both the activation energy E_a and the bonding energies E_s can be a distributed function of energy levels, whereby the surface B provides the reagent such bonding sites whose activation energies are distributed over the range from $E_a(min)$ to $E_a(max)$ and whose bonding energy is distributed over the range from $E_s(min)$ to $E_s(max)$.

In the case of a distributed function of activation or bonding energy, the reaction temperature can be utilized for controlling the saturation level

within the limits determined by the distributed energy functions.

On the basis of the above-discussed grounds, an advantageous embodiment of the invention is characterized in that the reaction temperature is set to a level at which the reagent introduced into the reaction space reacts so as to form a stable bond to the bonding site with only a portion of all those bonding sites which are in principle available within the temperature span confined by the upper and lower temperature limits. Advantageously, the temperature is set to a level at which the reagent introduced into the reaction space reacts with bonding sites having at least two different activation energies.

According to another preferred embodiment of the invention, the temperature is set to a level at which the reagent introduced into the reaction space reacts with bonding sites having mutually identical activation energies.

As noted in the general part of the description above, the number of surface-bond sites participating in the reaction which forms the stable end product is affected, besides by the control of the reaction temperature, also by the type of reagent selected. Consequently, according to a preferred embodiment of the invention, the reagent is selected such that the reagent introduced into the reaction space reacts with only a portion of the bonding sites available at the set reaction temperature, whereby a stable reaction product is formed with the reagent. To accomplish this, a reagent is selected, for instance, that reacts with chemically identical surface-bond sites only. One kind of these reagents are those that can react solely with the hydroxyl groups of the surface such as chromyl halides. According to another alternative embodiment, a reagent of large molecular size is selected whose molecules do not fit to bond to adjacent sites. Bonded to the surface, such a molecule will block the adjacent bonding sites of the surface thus preventing other molecules from bonding to said sites.

The invention is next examined in detail with the help of a detailed description and working examples. It must be noted that the description given below illustrates only a few preferred embodiments of the invention. Without departing from the scope and spirit of the invention, however, embodiments differing in their details from those described below are possible.

Fig. 1 shows the titanium content of Ti/alumina catalysts as a function of reaction cycles when the number of bonding sites on the support material surface are varied by repeated surface-bond reactions.

Figs. 2a to 2d show the structures determined by XRD of Ti/alumina catalysts prepared at four

different temperatures.

Fig. 3 shows the amount of chromium bonded to silica gel from different chromium reagents as a function of temperature.

Complementing the text above, an overview is given for the different control methods that can be employed in the reaction to attain a desired content of the active metal species in a catalyst prepared using the surface-bond selective method. The same control methods can also be utilized to change the concentration of additives or ligands used for modifying the properties of the catalytically active point.

A: The reaction temperature can be altered so as to attain desired conditions for bonding to the surface sites.

B: The surface properties can be modified by:
- an inhibiting reagent which deactivates a portion of the available bonding sites,
- a reagent which increases the number of available bonding sites, and
- a repeated sequence of surface-bond reactions which alter the chemical properties of the support material surface.

C: The reagent properties can be affected by:
- the selection of reagent molecules of different chemical properties, and
- the selection of reagent molecules of different size.

A. Reaction temperature:

The potential energy of the support material bonding sites varies according to the bonding site and its immediate surroundings. The metal compound introduced into the reaction space in gaseous form requires a certain energy to form a chemical bond with the desired bonding site. Elevation of the reaction temperature increases the available energy, whereby bonds of higher bonding energy can be formed. When the temperature is increased, also the desorption rate of the metal species from the support material surface begins to increase. Thus, a temperature window can be determined by experimental methods for a bonding reaction, whereby the lower temperature limit is set by the condensation temperature of the metal compound and/or the temperature necessary to exceed the reaction energy threshold and the upper temperature limit is set by either the decomposition temperature of the reagent or the temperature at which significant desorption of the reagent species starts to occur.

Further possibilities within this temperature

window are available through selective steering of the bonding of the metal compound to all available bonding sites, or alternatively, only to sites which exhibit a bonding energy above a certain threshold or an activation energy remaining below a certain threshold.

As an example, the bonding of $TiCl_4$ to a silica support at different temperatures is described (Example 1).

B1. Use of inhibiting reagent:

The bonding sites can be selectively filled using an inert molecule species with respect to the catalyst bonding reaction such that is capable of deactivating bonding sites of a certain energy. Then, the molecule to be reacted has less bonding sites available, whereby the metal content of the catalyst is reduced. After the metal compound has been reacted, the inhibiting reagent can be removed or chemically converted to a different form if its presence could disturb the reaction to be catalyzed, or alternatively, the bonding sites can be filled with another catalytically active metal species if desired.

As an example, the use of hexamethyl-disilazane as the inhibiting reagent prior to the bonding of chromium acetylacetonate on silica support is described (Example 2).

B2. Use of enhancing reagent for increasing the number of bonding sites:

The number of bonding sites can also be enhanced by chemical means using an appropriate reagent. Such a reagent can be, e.g., water vapour which is reacted with the support material surface at a certain temperature. In this reaction the surface attains a stabilized density of OH groups determined by the temperature used and the properties of the surface. If, during the preparation of a bimetal catalyst, for example, the content of the first metal to be reacted with the surface is desired to be affected, the number of bonding sites containing OH groups or other binding sites is reduced by thermal treatment, and then the first metal compound is introduced. Next, the surface is subjected to treatment by water vapour, and new OH group serving as bonding sites for the second metal compound will be created. The number of OH groups created depends on the water vapour treatment temperature.

Also, it will be possible to get more of the second metal bonded to the surface if, by removing the ligand of the first metal compound, the bonding sites which were in the "shadow" of the ligand tail become available.

Essentially, the example also includes another

method for increasing the number of bonding sites containing OH groups. If the first compound reacted with the surface is a metal halide, the halide ions are replaced by OH groups during the water vapour treatment, with a simultaneous release of hydrogen halides. Thus, new bonding sites are created for bonding the second reagent containing a metal compound.

B3. Modification of support material surface by repeated surface-bond reactions:

The number of bonding sites available on the support material surface can be affected by varying the chemical properties of the surface by way of repeated surface-bond reactions prior to the bonding of the actual catalytically active reagent. This modification process requires alternating repetition of at least two different surface-bond reaction cycles performed once or several times in such a manner that saturation of the surface is attained during each reaction cycle.

Typically, one of the reactions is such that occurs between the metal-containing reagent and the surface.

Following this reaction, a single or multiple reaction steps can be carried out in order to remove possible extra groups from the reagent chemically bonded to the surface or to create new bonding sites for the following process steps. New bonding sites can be created when, for instance, ligands are removed from the bonded reagent, whereby those bonding sites of the original surface that were shadowed by the ligands are revealed. New bonding sites can also be created in an exchange reaction between the bonded reagent and the reagent of the next process step, whereby the alternation of the reaction steps can form a compound such as oxide or nitride, for instance. The crystalline configuration of the formed compound can in certain cases be affected by selective choice of the bonding sites on the unbonded support material surface (through pretreatment) and control of reaction temperature so as to favour certain types of reactions. Thus, for instance, if $TiCl_4$ vapours are reacted with a silica support at temperatures below approx. 250 °C, an amorphous structure will be obtained, whereas temperatures in the range from 350 °C to 550 °C will give rise to catalysts with anatase TiO_2, anatase and rutile TiO_2, and rutile TiO_2 surface structures, respectively. The properties of the catalysts vary to some extent depending on the crystallinity of the catalysts, the amorphous structure being preferred for some applications.

As examples of the surface modification process prior to the reaction of the actual reagent, the deposition of aluminium oxide (Example 3) and

titanium oxide (Example 4) onto silica support is described.

C1. Different types of reagent molecules:

Molecules exhibiting different chemical properties in their reactions yield different contents of the catalytically active metal.

For instance, chromyl chloride (CrO_2Cl_2) and chromium acetylacetonate ($Cr(acac)_3$) bond to different bonding sites. Chromyl chloride reacts with the hydroxyl groups of the surface, whereby 1 or 2 HCl molecules per bonded Cr atom are released. By contrast, $Cr(acac)_3$ reacts with bonding sites containing hydrogen-bonded groups, whereby one of the three ligands is detached. Using chromyl chloride, the Cr content on silica support can be varied in the range from 1.8 to 5 wt % , and using chromium acetylacetonate, in the range 0.6 to 2.4 wt % when preheating of the silica support is carried out in a temperature range from 820 °C to 200 °C, respectively.

The $WOCl_4$ and WCl_6 molecules have approximately equal size, yet their bonding to surface-bond sites is different. An example of this is the bonding of tungsten onto alumina from $WOCl_4$ and WCl_6. The reaction takes place with the hydroxyl groups of the surface in the form of an exchange reaction, whereby 1 or 2 HCl molecules are released per each bonded W-species molecule.

The above-discussed reactions are illustrated in Examples 5 and 6.

C2. Size of reagent molecule:

Besides the chemical properties of a molecule, its size can affect the saturation level. Metal compounds of different molecular size give a possibility of controlling the mutual distance of the catalytically active species. Increase of the molecular size permits the outdistancing of the metal atoms, because the condensation of a metal compound onto an already bonded compound under saturation conditions at a sufficiently high reaction temperature cannot occur (refer to Example 7). Example 7 is a partial extension of Example 5. On reason for the different saturation level behaviour obviously is, besides the differences in the chemical properties, the difference in the molecular sizes, because the relative proportions of hydroxyl groups and hydrogen-bonded groups at the 450 °C reaction temperature of the example on the support material surface are approximately equal.

Example 1:

Effect of reaction temperature

SiO_2 was pretreated for 16 h at 450 °C in air atmosphere and for 4 h in nitrogen at 70 mbar pressure. The silica support (7 g) was heated in nitrogen at 70 mbar pressure up to the reaction temperature which was 175 °C, or alternatively, 450 °C. $TiCl_4$ vapour was introduced for 2 h into the reaction space using nitrogen gas as carrier. The silica support was flushed with nitrogen gas for 2 h at the reaction temperature and cooled. The Ti content on the silica support was determined. The Ti contents were 3.3 wt % subsequent to the reaction at 175 °C and 2.6 wt % subsequent to the reaction at 450 °C. Also the Cl/Ti ratio changed from 2.8 to 2 when the reaction temperature was elevated from 175 °C to 450 °C. This indicates that the bonding of $TiCl_4$ to two OH groups is enhanced at the higher reaction temperature. At 175 °C, a major portion of the $TiCl_4$ bonds to one OH group.

Example 2:

Utilization of inhibiting reagent

SiO_2 was heated for 16 h at 820 °C in air atmosphere and for 4 h at 450 °C in a partial vacuum flushed with nitrogen gas. The temperature was lowered to 175 °C. Vapourized hexamethyl-disilazane at 50 °C temperature was introduced into the reaction space and reacted at 175 °C with the silica support. The excess reagent was flushed with nitrogen gas at 175 °C. The temperature was elevated to 200 °C and $Cr(acac)_3$ was reacted for 3 h with the silica support treated in the above described manner. The silica support was finally flushed with nitrogen at 200 °C.

A reference sample was prepared by bonding chromium from $Cr(acac)_3$ alone under the same conditions as above. The chromium content of the reference sample was 0.65 wt %, while in the sample treated with the hexamethyldisilazane, the corresponding content was only 0.08 wt %.

Example 3:

Surface modification by repeated sequence of surface-bond reactions

Layers of Al_2O_3 can be grown on silica by flushing the pretreated silica support alternatingly with $AlCl_3$ and H_2O, both in vapour phase. The reaction can be carried out over a wide temperature range, whereby the growth rate of Al_2O_3 is dependent on the reaction temperature. When Al_2O_3 was deposited on silica at 200 °C, the use of 1, 2 and 3 reaction cycles increased the Al concentration to 0.58, 1.0, and 1.7 % by weight after the first, second and third reaction cycles,

respectively. When using 420 °C reaction temperature, the following Al concentrations were obtained after 1, 2, 3, 4 and 6 reaction cycles: 0.31, 0.66, 1.0, 1.3 and 2.0 % by weight.

Example 4:

Surface modification by repeated surface-bond reaction cycles

An oxide layer corresponding to Al_2O_3 can be grown on pretreated silica using $TiCl_4$ and H_2O, both introduced alternately in vapour phase. Here also, the growth rate is dependent on the reaction temperature.

Fig. 1 illustrates the Ti content when the TiO_2 is grown using 1 and 2 reaction cycles at 200 °C and 450 °C.

Furthermore, the structure of TiO_2 thus grown can be altered by changing the reaction temperature.

Thus, silica carriers were pretreated for 16 h at 560 °C in air and for 4 hours *in vacuo* at a temperature corresponding to the reaction temperature in a nitrogen atomsphere. After the pretreatment, $TiCl_4$ vapours were reacted with silica at four different temperatures, viz., 250 °C, 350 °C, 450 °C and 550 °C, the reaction time being 2 hours. Finally, the samples were flushed with a stream of nitrogen at the reaction temperature. The Ti contents of the samples were determined, as were the structure of the samples by XRD. The XRD analysis results are depicted in figures 2a to 2d. The figures show that a change of reaction temperature from 250 °C to 550 °C had a clear impact on the structure of the catalysts, a transition from an amorphous surface structure via an anatase TiO_2 surface structure at 350 °C, a mixed anatase + rutile TiO_2 surface structure at 450 °C to a rutile TiO_2 surface structure at 550 °C being noticeable. In the figures, the anatase phase has been desinated the letter A and rutile the letter R.

Example 5:

Use of reagents exhibiting differing chemical properties

A set of SiO_2 support material samples were pretreated at different temperatures for 16 h in air atmosphere and further for 4 h in 70 mbar vacuum at either the pretreatment temperature or at 450 °C when the pretreatment had been carried out at 450 to 820 °C. Approx. 7 g of SiO_2 was heated in nitrogen gas atmosphere to the reaction temperature which was 220 °C. Chromyl chloride was reacted for 3 h with the silica, after which the silica was flushed with nitrogen gas at the same tem-

perature. In another set of samples the reagent was vapourized Cr(acac)₃ which was reacted for 3 h with the silica. The chromium contents were determined for both sets of samples. These contents as a function of pretreatment temperature are illustrated in Fig. 2. The chromium contents can be varied as a function of temperature, but the attained saturation level varies according to the different reagents used.

Example 6:

Use of reagents exhibiting different chemical properties

Al_2O_3 (Grace, surface area 280 m²/g, particle size 0.5 to 1.0 mm) was heated for 16 h at 420 °C in air atmosphere and for 3 h in a partial vacuum flushed with nitrogen gas. Vapourized WCl_6 was reacted with aluminium oxide for 4 h at 420 °C. A corresponding reference sample was prepared using $WOCl_4$ as the reagent. The W species content in both samples was determined and the saturation level was measured as 2.3 wt % when using WCl_6 as the reagent and 3.6 wt % when using $WOCl_4$ as the reagent. The different levels of saturation can plausibly be attributed to the different chemical properties of the reagents used.

Example 7:

Use of reagents of different molecular sizes

SiO_2 was heated for 126 h at 450 °C in air atmosphere and for 4 h in vacuum (nitrogen gas atmosphere). Chromyl chloride was reacted at 200 °C with the silica, after which the saturation level of Cr was determined to be 3.7 wt %, or 1.4 Cr atoms per nm². Chromium acetylacetonate reacted at 200 °C with similarly pretreated silica yielded a saturation level of 1.4 wt %, or 0.54 Cr atoms per nm². Thence, the use of chromyl chloride yields a 2.6-fold content of Cr over chromium acetylacetonate. The surface ratio of chromyl chloride molecules to chromium acetylacetonate molecules is 1:3.6.

Claims

1. A method for preparing a heterogeneous catalyst comprised of a support material and at least one catalytically active species, according to which method

   - a reagent containing a catalytically active species or its precursor is introduced into a reaction space where it is reacted in vapour phase with the support material surface,

characterized in that

   - the reaction temperature is set at such a level at which the number of the surface-bond sites which as determined by the set reaction temperature, introduced reagent and chemical structure of support material surface are available for preparing a stable surface-bonded product when the reagent is reacted with the support material surface, at least approximately corresponds to the desired content of the catalytically active species in the catalyst being prepared and

   - at least essentially all of the available surface-bond sites are reacted with the introduced reagent by maintaining the vapour pressure of the catalyst reagent sufficiently high and the time of interaction between the reagent and the support material sufficiently long as to keep the quantity of reagent molecules coming into interaction with the support material surface at least as large as the quantity of said surface-bond sites available on the support material,

   the lower limit of the set reaction temperature being the vapourization temperature of the reagent under the conditions of the reaction space and the upper limit being the temperature at which the reagent begins to decompose chemically in significant quantities in the gas phase.

2. The method as claimed in claim 1, characterized in that the reaction temperature is set to a value at which only a portion of all those surface-bond sites of the support material which in principle are available within the temperature span between the upper and lower limits of the viable reaction temperature so as to form a stable reaction product with the introduced reagent.

3. The method as claimed in claim 2, characterized in that the reaction temperature set to a level at which surface-bond sites of mutually equal activation energy react with the introduced reagent.

4. The method as claimed in claim 2, characterized in that the reaction temperature is set to a level at which surface-bond sites of at least two different activation energy levels react with the introduced reagent.

5. The method as claimed in any of the previous claims, characterized in that the number of surface-bond sites available on support ma-

terial surface is altered prior to the introduction of the reagent by treating the surface with an inhibiting reagent capable of deactivating at least a portion of the bonding sites on the support material surface.

6. The method as claimed in any of claims 1 to 4, **characterized** in that the number of surface-bond sites available on support material surface is increased prior to the introduction of the reagent by chemically treating the surface with a suitable reagent.

7. The method as claimed in claim 6, **characterized** in that the reagent used is water vapour.

8. The method as claimed in any of claims 1 to 4, **characterized** in that the chemical properties of the support material surface are modified by repeated cycling of surface-bond reactions prior to the reaction between the catalytically active reagent and the surface.

9. The method as claimed in any of the previous claims, **characterized** in that the reaction temperature is selected according to the desired degree of crystallinity of the catalytically active species bonded to the surface of the support.

10. A method for preparing a heterogeneous catalyst comprised of a support material and at least one catalytically active species, according to which method
    - a reagent containing a catalytically active species or its precursor is introduced into a reaction space where it is reacted in vapour phase with the support material surface,
    characterized in that
    - the reagent introduced into the reaction space is selected so that the number of the surface-bond sites which as determined by the set reaction temperature, introduced reagent and chemical structure of support material surface are available for preparing a stable surface-bonded product when the reagent is reacted with the support material surface, at least approximately corresponds to the desired content of the catalytically active species in the catalyst being prepared and
    - at least essentially all of the available surface-bond sites are reacted with the introduced reagent by maintaining the vapour pressure of the catalyst reagent so high and the time of interaction between the reagent and the support ma-

terial so long that the quantity of reagent molecules coming into interaction with the support material surface is at least as large as the quantity of said surface-bond sites available on the support material.

11. The method as claimed in claim 10, **characterized** in that the introduced reagent is selected so that only a portion of all those surface-bond sites of the support material which in principle are available at the set reaction temperature can react so as to form a stable reaction product with the reagent.

12. The method as claimed in claim 10, **characterized** in that such a reagent is selected that reacts only with surface-bond sites of mutually similar chemical properties.

13. The method as claimed in claim 11, **characterized** in that such a reagent is selected that reacts only with the hydroxyl groups of the support material surface.

14. The method as claimed in claim 10, **characterized** in that such a reagent is selected whose molecules, by their large molecular size, cannot bond to adjacent surface-bond sites.

15. The method as claimed in any of the previous claims, **characterized** in that the reaction between the reagent and the support material surface is carried out in a static column of the support material, an inert gas flow containing the reagent being routed via the column at a flow rate which at least essentially corresponds to the diffusion rate of the reagent into the pores of the support material under the reaction conditions.
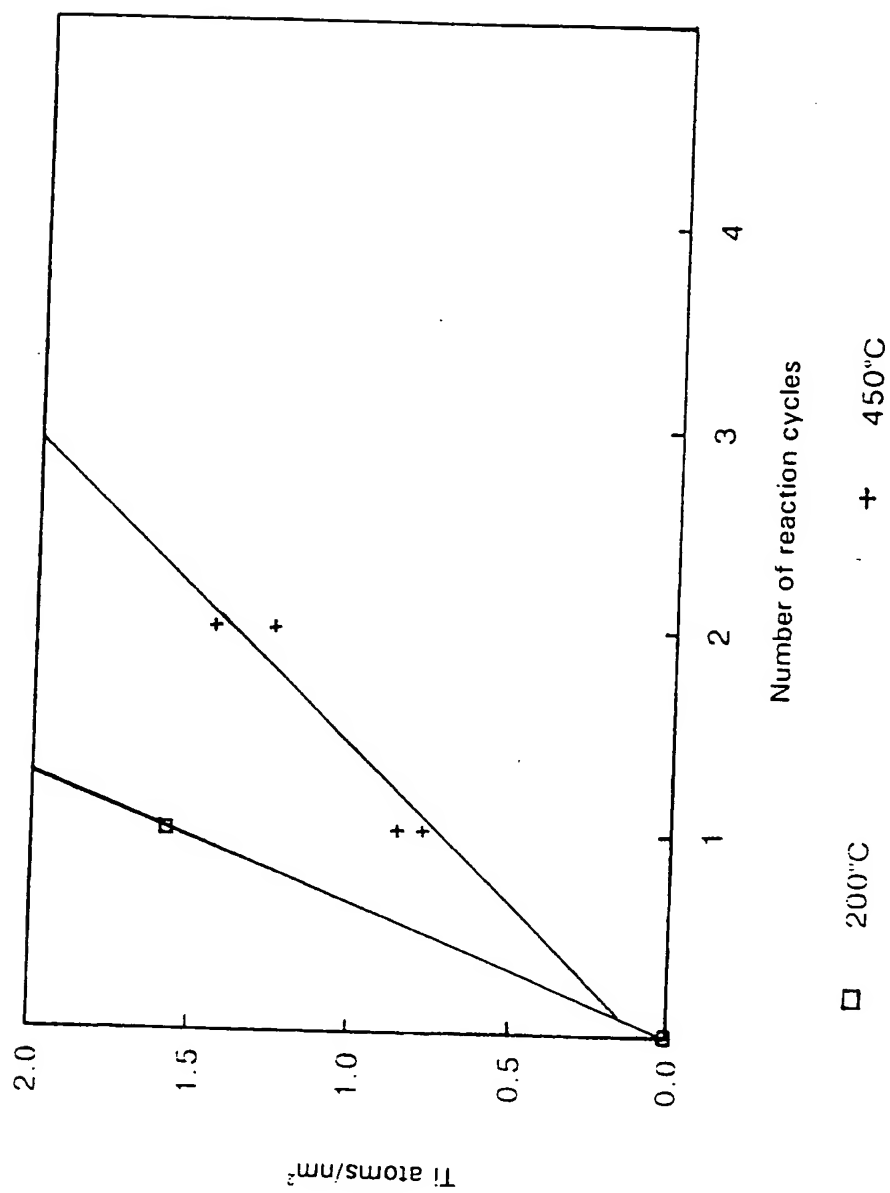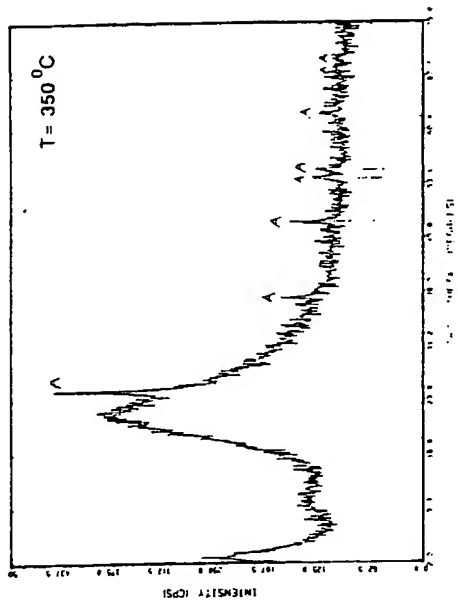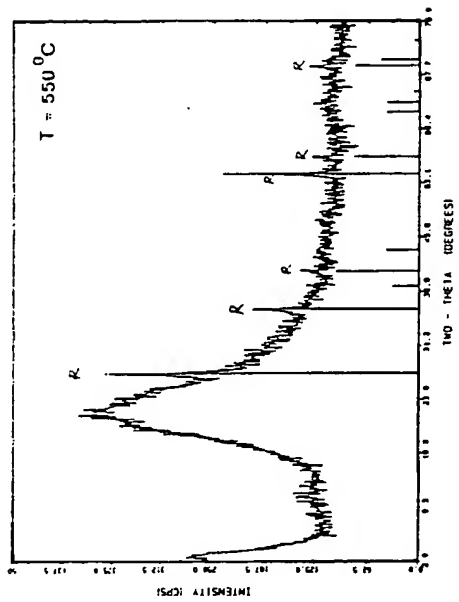
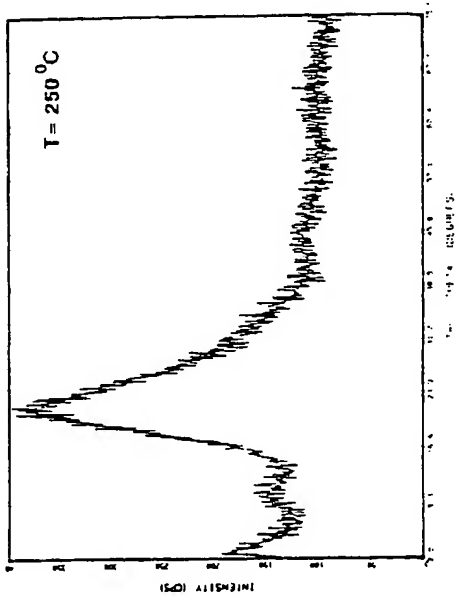Fig. 1 Content of Ti species in TiO₂ layers.

Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2d
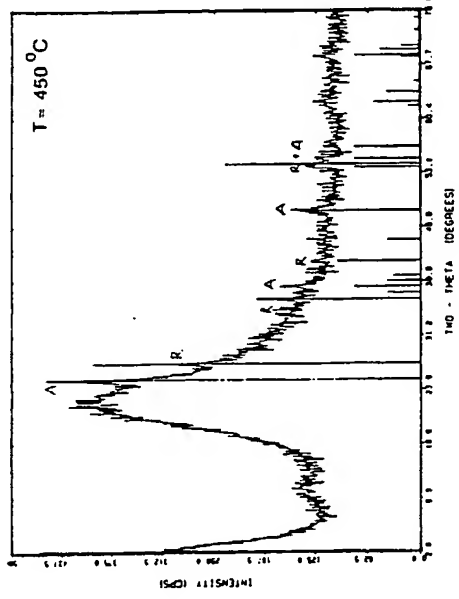
Fig. 3   Cr bonded from chromium oxychloride and acetylacetonate.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 438 134 (NESTE OY) * claim 1 * ---	1	B01J37/02
A	EP-A-0 156 424 (SHELL) ---		
A	US-A-4 670 411 (T. JOHNSON) ---		
A	US-A-4 459 372 (B. ARENA) -----		

	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
	B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 NOVEMBER 1992	THION M.A.

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